Recent advances in electrode design from one-dimensional nanostructure arrays for proton exchange membrane fuel cell applications

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Recent advances in electrode design from aligned one-dimensional nanostructures for proton exchange membrane fuel cells

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Abstract

The anisotropic morphology and unique surface properties of one dimensional (1D) nanostructured catalysts endow them outstanding catalytic performance toward oxygen reduction reaction (ORR). Recent development in 3D ordered nanostructures from aligned 1D catalysts has seen a large potential to really make them into practical electrodes for proton exchange membrane fuel cell (PEMFC) applications. This new technology is expected to address the mass transfer and durability challenges faced current Pt/C electrodes for the development of next generation PEMFCs. In this review, we systematically describe our recent advancements in 3D ordered electrodes from self-standing aligned Pt nanowires. Nanostructured thin film (NSTF) catalysts and electrodes from Pt-based nanoparticle decorated aligned polymer nanowires, carbon and TiO_2 nanotubes are also discussed. The progress of electrodes from aligned Pt-based nanotubes is reviewed as well. Finally, challenges and future developments of aligned 1D nanostructured electrodes are addressed.

Keywords: PEMFC, 1D, ORR, electrode, catalyst, ordered nanostructure

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is an electrochemical energy conversion device which can directly convert the chemical energy in fuels (i.e. hydrogen) to electricity by a one-step electrochemical reaction with oxygen. This is a clean process with high energy efficiency and the by-products are only water and heat. Operating usually between room temperature and 80^{o}C, the PEMFC has an electricity efficiency of 40-50% and a combined energy efficiency of 80-95% if the heat can also be used (i.e. in combined heat and power, CHP) [1]. PEMFCs have advantages of solid state-based compact design, fast start-up and shutdown, and flexible power scales. The first PEMFC unit was developed in 1960s at General Electric (GE) for spacecraft, and significantly improved in 1980s and 1990s by introducing carbon supported Pt nanoparticle (Pt/C) electrocatalysts and proton conducting ionomer in the catalyst layer, which significantly reduced the Pt loading amount in electrodes with enhanced fuel cell power performance [2]. Today, PEMFCs have been successfully applied in transports and buildings, including the first released commercial PEMFC-based vehicles Toyota Mirai in 2014 which has been sold nearly 10 000 across the world. However, the system cost and durability are still the two major challenges faced the PEMFC applications today (Fig. 1(a)) [3]. They are still far below enough to competitive with currently well developed technologies, e.g. internal combustion engines (ICE) and batteries. Among all PEMFC components, the electrode is the place where the electrochemical reactions take place. It determines the fuel cell performance and costs more than half of the total fuel cell stack (Fig. 1(b)) [3]. Therefore, to move PEMFCs to extensive commercial applications, it is necessary to develop high performance, low cost and reliable electrodes to fulfil the sustainable requirements for practical applications.

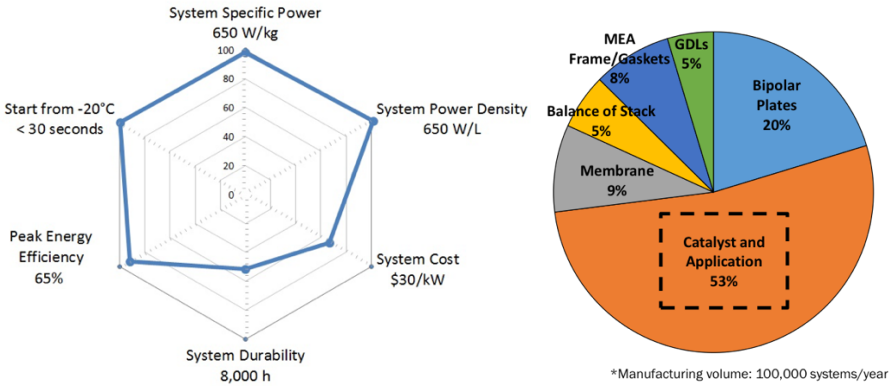

Fig. 1. The status of current PEMFC development and stack cost breakdown based on DOE Review 2019. Reproduced from Ref. [3] with permission of D. Papageorgopoulos.

2. Catalyst electrodes from aligned one-dimensional nanostructures

In the conventional PEMFC electrode, the catalyst layer is constructed from randomly arranged Pt/C nanoparticles with proton conducting ionomer as both binder and ion transfer network. The electrode structure provides some porosity between Pt/C nanoparticles for transferring reactant gases and produced water, as well as carbon network for electron transfer and ionomer path for proton moving. The active site with all three functions is usually called triple phase boundary (TPB). Within the Pt/C catalyst electrodes, this disorganized structure limits the charge and mass transfer usually resulting in a low catalyst utilization ratio (usually below 30%) and restricting the large current density operation of fuel cells in practical applications. A summary of the challenges with the conventional Pt/C electrodes was very recently reviewed in Yang's work [4].

To address these challenges, the concept of three-dimensional (3D) electrodes from aligned one-dimensional (1D) catalyst nanostructures was developed with a super-high degree of active site exposure and high-efficiency mass transfer path within the extremely thin catalyst layer. It is regarded as the most promising approach to significantly boost catalyst utilization ratio and power performance. An ideal electrode model from aligned 1D nanostructures was proposed by Middelman in 2002 as shown in Fig. 2 [5]. It is expected the structure can be built

with a vertically oriented catalyst-coated electron conductor, vertically oriented proton conductor and vertically oriented through-hole structure. In recent decades, various electrode types from aligned 1D nanostructures have been reported based on catalyst decorated aligned nanowires or nanotubes, or even self-standing aligned 1D metal catalysts.

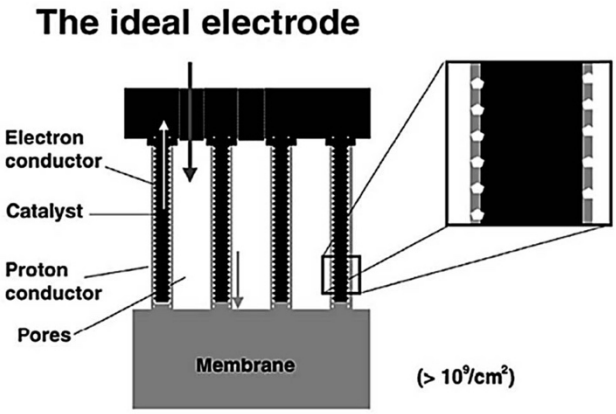

Fig. 2. Schematic diagram for the ideal electrode. Reproduced from Ref. [5] with permission of Elsevier, 2002.

3. Aligned 1D nanostructures as catalyst support

3.1 Nanostructured thin film (NSTF) catalysts

One of the significant electrode types from aligned 1D nanostructure comes from nanostructured thin film (NSTF) catalyst proposed by 3M Co. This catalyst electrode structure has been reviewed in a few papers by M.K. Debe [6,7]. It consists of a thin layer of polycrystalline thin film of Pt alloy (e.g. PtCoMn or PtNi) catalyst (0.05/0.1 mg_{Pt}/cm^2 at anode and cathode, respectively) coated by magnetron sputter on aligned perylene based polymer whiskers with an average cross-sectional size of 55 nm x 30 nm less than 1 μm tall. The catalyst coated whiskers have a distribution density of 30-40 per square micrometer, forming nanosized hydrophilic pores between the walls of catalysts [8]. The total catalyst layer thickness is ca. 1 μm which is 10 to 20 times thinner than equivalently loader conventional Pt/C nanoparticle electrodes. This thin catalyst layer effectively enhances the proton and

electron transfer. Within this catalyst layer, Pt alloy covers the entire surface of the whisker support and the nanosized hydrophilic pores are typically flooded with water during operation which facilitates proton transport due to electrostatic interactions with the surface charges of the pore walls [9]. Therefore, proton conducting ionomer, which has been considered as one of the main degradation materials for the catalyst layer in operation, is thus successful mitigated from the NSTF catalyst, providing a potential to improve the durability. However, the large size of catalyst structure results in a low electrochemical surface area (ECSA) in the range of 10 to 25 m^2/g which is smaller compared to high surface area Pt/C catalysts [8], although this could be partially compensated by the 5 to 10 fold gain in specific activity to achieve reasonable mass activity. Another very major consequence of the extreme thinness of the NSTF catalyst layer is the flooding issue. At a given current density, the water generation rate per unit thickness on the cathode is 20 to 30 times higher for an Pt/C electrode proportionately thinner. This brings in a big challenge for water management strategies. These issues finally make this promising NSTF technology still difficult to be put into real applications.

Similar to the aligned polymer whiskers used in the NSTF catalyst, aligned conductive polymer nanowires, such as polypyrrole (PPy) and polyaniline (PANI) have also been investigated as catalyst supports for Pt nanostructures. The low cost of PPy and PANI, combined with their reasonable conductivity in partially oxidized state, high chemical stability in acid medium, good thermal conductivity, as well as its facile to be constructed in ordered nanostructure, e.g. aligned nanowires or nanotubes, make them appealing electrocatalyst supports for PEMFC application. Shao's group prepared electrodes from PtPd decorated aligned PPy nanowires [10]. PPy nanowires were grown on Pd nanoparticle modified steel stainless plate, on the surface Pd and then Pt were decorated by physical vapor deposition (PVD). The PPy nanowire exhibited a conical structure with an average diameter of approximately 120 nm at the bottom and 80 nm at the top, with the average length of about 1.1 μm and average distance between two adjacent nanowires of about 60 nm. The PtPd catalyst thin layer showed whiskerette shapes formed along the long axis of the PPy nanowires. The resulting structures were hot-

pressed onto the polymer electrolyte membrane (PEM) to construct a membrane electrode assembly (MEA) without using proton conducting ionomer (similar to the NSTF catalyst). The single cell exhibited a maximum power density of 762.1 mW cm^{-2} with a Pt loading of 0.241 mg_{Pt} cm^{-2} (anode + cathode). A similar work has also been conducted by Sun's group to grow aligned PPy nanowires directly on carbon paper gas diffusion layer (GDL) substrate (Fig. 3) [11]. Also, the nanowires were grown under the existing of proton conducting ionomer which successfully doped into the matrix of PPy molecular chains. Pt ions were then deposited onto nanowire surface driven by the electrostatic interactions between Pt cations and sulfonate groups of ionomer. Finally, Pt ions were reduced to form Pt nanoparticles using hydrogen at 250°C. The achieved Pt nanoparticles had an average size of 4.3 nm with well-defined spherical nano-crystallines uniformly distributed on the surface of the PPy nanowires. The unique electrode structure finally showed a higher cathode mass specific power density of 11.97 W $mg_{Pt\ cathode}^{-1}$. Sun's group also reported electrodes from aligned PANI nanowires decorated with Pt nanoparticles and whiskers for PEMFC applications [12,13]. Aligned PANI nanowires were first grown on GDL. The length and diameter were controlled via altering the concentration of aniline monomer or the reaction temperature during the in-situ polymerization process. Typically, they possessed an average diameter of 61 nm, an average length of 194 nm, and a growth density of 78 μm^{-2}. The electrodes were then obtained by either spraying catalyst ink or sputtering Pt using the PVD method. In case of PVD, the average thickness of the deposited Pt layer is about 8.9 nm. The layer also consists of Pt crystalline nanowhisker arrays (NWAs) along the axial direction of the aligned PANI nanowires, which is similar to the catalyst structures obtained by PVD in the NSTF catalyst and PtPd on PPy nanowires in Shao's work. Despite the Pt catalyst layer has a large size, with the aid of the improved mass transport within the aligned structure, this well-tailored electrode applied as the cathode of a PEMFC also achieved a cathode mass specific power density of 5.7 W $mg_{Pt\ cathode}^{-1}$ and 39% increase compared to that of Pt/C electrocatalysts (Pt/C 60 wt%, Johnson Matthey).

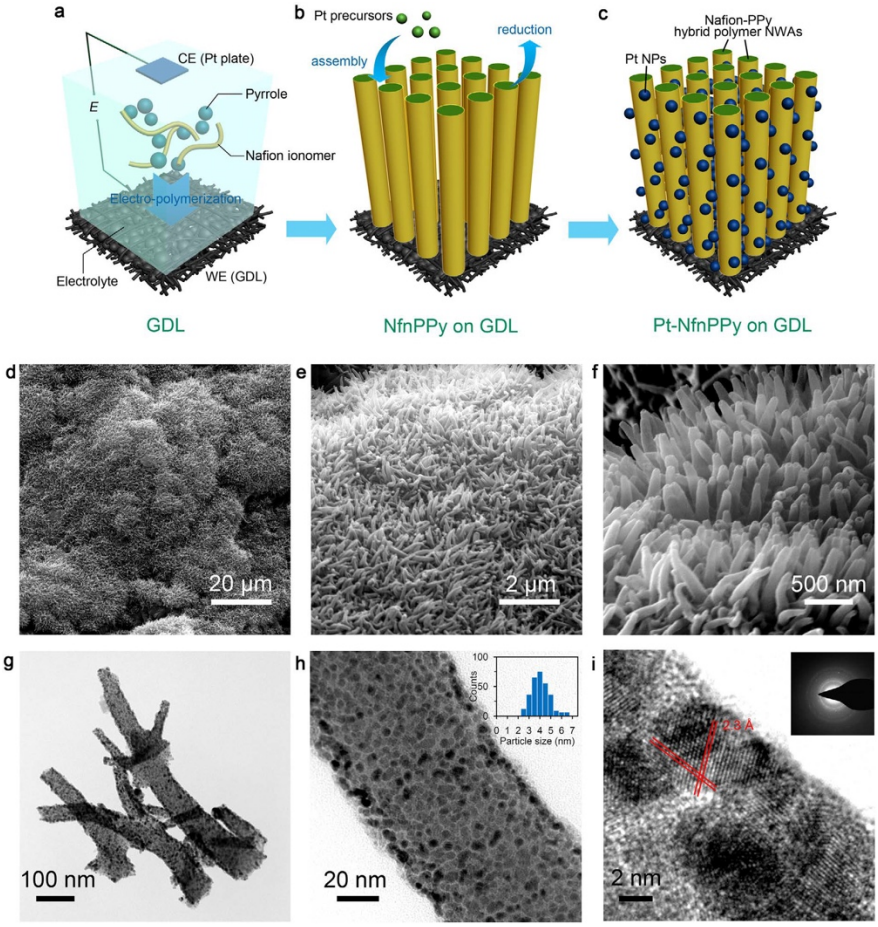

Fig. 3. (a–c) Synthetic scheme of the electrode from aligned PPy nanowires via electrochemical polymerization (a), Pt loading (b) and MEA fabrication (c). (d–f) SEM images of Pt-NfnPPy on the surface of a GDL at different magnifications. The rough surface of Pt-NfnPPy in a low magnification (d) represents the surface morphology of GDL built up with carbon powder. (g,h) TEM images of Pt-NfnPPy at different magnifications. Inset histogram of (h) is the Pt nanoparticle size distribution with an average size of 4.3 nm. (i) HRTEM image of Pt-NfnPPy with inset patterns of SAED. Reproduced from Ref. [11] with permission of Springer Nature, 2015.

3.2 Pt nanoparticles supported on aligned 1D nanostructure support

Taking the advantages of aligned 1D nanostructures, electrodes have also been developed by depositing Pt catalyst onto aligned carbon nanotubes (CNTs). CNTs possess better electrical conductivity and large surface area than the polymer whiskers, and the aligned CNT

structure can also benefit from the vertically oriented structure and continuous straight pore structure enabling better mass transportation in practical electrodes compared to high surface area carbon particles, as well as a high durability in fuel cell applications.

A typical fabrication process for the electrode from Pt decorated aligned CNTs is shown in Fig. 4. In general, aligned CNTs are grown on substrate surface (stainless steel, SiO_2, quartz, Al foil, etc.) with catalysts (e.g. Fe or FeCo), then the whole or top part of CNTs were decorated with Pt nanoparticles by chemical or physical methods followed by surface coating with proton conducting ionomer, finally the substrate with Pt decorated aligned CNTs is decal transferred onto PEM by hot pressing. Chen's group [14] demonstrated aligned CNTs (with an average height of 4 μm) decorated with 4 nm Pt nanoparticles by controlled chemical reduction from H_2PtCl_6 solution using $NaBH_4$ as the reductant, reporting a higher ECSA and double specific mass power density compared to the conventional Pt/C (HiSPEC™ 4000, Johnson Matthey) electrodes in the H_2/O_2 PEMFCs (78.72 to 52.22 $m^2\ g_{Pt}^{-1}$, and 1.43 to 0.70 kW g_{Pt}^{-1}, respectively). Tian et al. [15] reported a scalable approach combining plasma enhanced chemical vapor deposition (PECVD) and physical sputtering for fabricating MEAs with Pt-coated aligned CNTs. Aligned CNTs with the average length of about 1.3 μm and a diameter of about 10 nm were grown on Al foil. Pt nanoparticles were deposited using physical sputtering method achieving with a depth of about 200 nm. With a Pt loading of 0.035 mg cm^{-2}, the MEA from the Pt/aligned CNTs exhibited a comparable power performance to that from conventional Pt/C catalysts at a Pt loading of 0.4 mg cm^{-2} in H_2/O_2 PEMFC. Further development of Pt/aligned CNTs include the growth of thinner CNTs and the deposition of uniformly distributed extremely small Pt nanoparticles, and some of these works were summarized in the review paper by Van Hooijdonk [16-18].

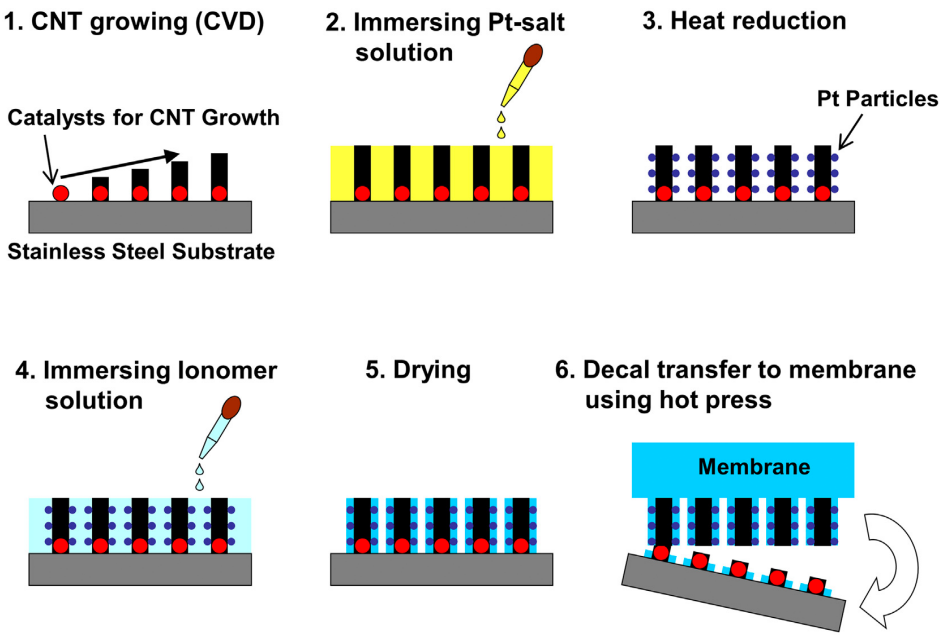

Fig. 4. Preparation procedure of aligned CNT electrodes. Reproduced from Ref. [16] with permission of Elsevier, 2014.

However, with the physical sputtering method, it's difficult to achieve a high Pt loading in practical electrodes without causing aggregation. With our group, we developed a facile approach with a high scalability by combining the aligned CNTs with 1D Pt nanostructures to overcome this obstacle [19]. Rather than using transferred substrate, aligned CNTs were directly grown on GDLs using PECVD technique and then the CNT surface was functionalized to increase the activity using active screen plasma nitriding (ASPN) to achieve aligned N-doped CNTs. Onto the aligned N-CNTs Pt nanorods were grown using a facile aqueous formic acid reducing method at room temperature (Fig. 5). Compared to the electrode with Pt/C nanoparticle catalysts, our electrodes with a half Pt loading showed an enhanced power density and better durability.

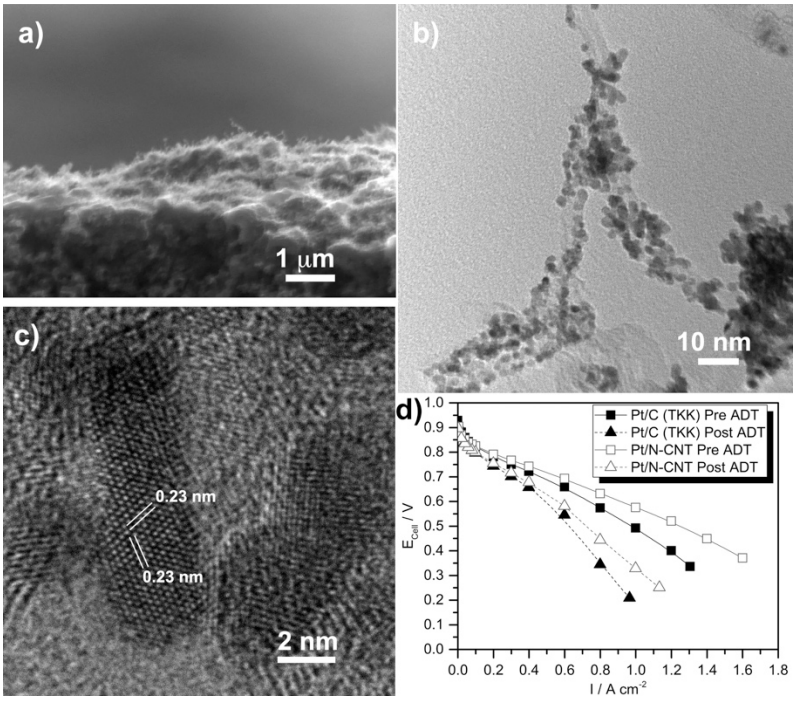

Fig. 5. (a) SEM image of the cross section of the N-CNT GDL. (b) TEM images of Pt supported on N-CNTs and (c) HR-TEM images of Pt nanorods demonstrating the inter-lattice spacing of single crystal Pt nanorods growing along <111> direction. (d) polarization curve comparison for the Pt/C and Pt/N-CNT electrodes before and after the accelerated degradation test (ADT). Reproduced from Ref. [19] with permission of Elsevier, 2020.

Although better than the active carbon support, the CNT still suffers from a poor tolerance to the electrochemical corrosion at a high potential in the start-up and long-term operation process of PEMFCs. Therefore, metal oxides, such as 1D TiO_2 nanostructures were explored for the application. Different to carbon materials, TiO_2 possesses a high corrosion resistance to oxidation and special interaction with metal catalysts as catalyst supports. Aligned TiO_2 nanotubes were prepared by electrochemical anodic oxidation followed by wet chemical reduction or PVD to decorate catalyst nanoparticles [20], which is very similar to the catalyst decoration onto the aligned CNTs. The main challenge with TiO_2 as the catalyst support is the relatively poor electronic conductivity. As a consequence, the resistance of the electrode with aligned TiO_2 nanotubes is about 10-fold greater than that of the conventional Pt/C electrode.

Therefore, to improve the electrical conductivity, TiO_2 nanostructures were annealed in a reducing gas atmosphere (e.g., H_2) to increase the density of oxygen vacancies and form donor states close to the conduction band, [21]. The electrical conductivity was markedly improved by almost one order of magnitude after hydrogen treatment leading to an improved power performance. Further improvement was realized by using carbon coated aligned TiO_2 nanorods and nanotubes, which have also been studied as catalyst supports for PEMFC applications [22,23].

4. Aligned 1D catalysts

4.1 Excellent activities of single crystal Pt nanowires

The stability of catalysts is confirmed to be one key factor in determining the fuel cell durability. As the most commonly used catalysts, the stability of Pt-based nanoparticles is still poor in PEMFC operation and can still not meet the requirements for practical applications (Fig 1(a)). Pt-based nanoparticles can degrade through a few mechanisms, including dissolution, aggregation and Oswald ripening, as well as detaching from the support, finally resulting in a low catalytic performance. The degradation processes of Pt-based nanoparticles on the nanoscale were summarized by Meier recently in his review paper [24]. During past three decades, many new catalyst nanostructures have been reported to overcome these challenges. The advance in material synthesis and nanotechnology brought in tremendous progress to the development of fuel cells, in particular the understanding of fuel cell catalytic reactions and the mechanisms on catalysts. Chorkendorff et al. compared various latest fuel cell catalysts reported based on their mass activities towards oxygen reduction reaction (ORR) in liquid half cell electrochemical measurement and in fuel cell testing (Fig. 6) [25]. Among them, ultrathin jagged nanowires with a diameter of about 2.2 nm, prepared by fully leaching Ni from PtNi nanowires forming rough surface, show the highest catalytic activity of 13.6 A mg_{Pt}^{-1} at 0.9 V, which is 52 times that of Pt/C (0.26 A/mg_{Pt}, 10 wt_{Pt}% on carbon) nanoparticle catalysts [26]. Combining with the high electrochemical surface area (ECSA) of 118 m^2 g_{Pt}^{-1},

jagged Pt nanowires are therefore considered as the most promising catalysts for fuel cell applications and attracting huge effort from fuel cell researchers and manufacturers.

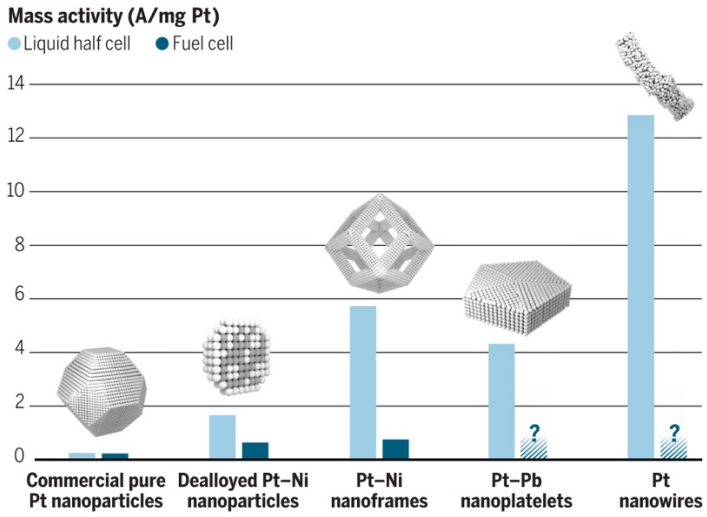

Fig. 6: Mass activity comparison of various latest fuel cell catalysts by liquid half cell electrochemical measurement and fuel cell test. Reproduced from Ref. [25] with permission of AAAS, 2016.

Comparing with their zero-dimensional (0D) counterparts, 1D metal nanostructures, in particular 1D single crystal metal nanostructures exhibit several advantages, such as high specific surface activity due to the preferential exposure of high active crystal facets, facilitating the electron transport by the path directing effects in catalyst layers, and good stability to alleviate the dissolution, Oswald ripening and aggregation because of the asymmetric structure. A comparison of nanoparticles with 1D nanostructures for fuel cell applications has been recently summarized by our group in one review paper [27].

However, it still remains a big challenge to translate the full extent of the superior performance of the latest generation of fuel cell catalysts to PEMFC devices. There are two large difficulties to really apply high performance 1D nanostructure catalysts into practical fuel cell applications: i) scaling up the synthesis process to fulfil the large amount requirement in fuel cell applications. For example, PtNi nanoframes and jagged Pt nanowires were both synthesized

using organic solvent oleylamine (OAm) process. The synthesis yield of the reaction is not very high and the separation of the product from the reaction system is sophisticated. For laboratory scale preparation and half cell electrochemical measurement, an amount at micro gram level is accepted. But, for the application in fuel cells, catalyst in gram scale is necessary, and this becomes highly challengeable for controlling the complex synthesis process to obtain high quality materials; and ii) as 1D catalysts, the nanostructures have different morphologies with a larger aspect ratio than spherical Pt/C nanoparticles. Thus, the electrode fabricated using the conventional method optimized for Pt/C nanoparticles (coating from the catalyst ink) cannot turn the outstanding catalytic properties of 1D catalysts to high performance electrodes. In the half cell measurement in liquid electrolyte, a thin film electrode with rotating disk electrode (RDE) method is used. It is in a clean environment with ignored mass transfer influence. But in operated fuel cells, the situation is severe and complex, where mass transfer problems including moving reactant gases to reaction sites and transferring generated water outside also become a key factor at the large current density operation [28,29]. So, new electrode structure platforms, e.g. 3D nanostructures from the aligned nanowires, are required to really bridge the gap between the well developed 1D catalysts with high power performance fuel cell devices.

4.2 Electrodes from aligned single crystal Pt nanowires

The synthesis of single-crystal Pt nanowires can be achieved by polyol process, but surfactants, such as PVP, are usually required to induce the growing of Pt. Another method using organic solvent, oleylamine process, has also attracted a lot of efforts. There is no surfactant or ligand needed in the reaction, thus a clean nanowire can be obtained. However, in addition to the complex process, a high reaction temperature is also necessary for this reaction in organic solvents. In comparison, formic acid reduction approach is facile and can be conducted in aqueous solution at nearly room temperature to grow nanowires, thus it can

be counted as a green chemical process for material synthesis [30-32]. A detailed discussion and comparison of various methods for Pt-based nanowire preparation can be found in [33,34].

4.2.1 Gas diffusion electrodes from aligned single crystal Pt nanowires

Gas diffusion electrodes (GDEs) from aligned single crystal Pt nanowires were first reported by our group in 2010 [35]. With the GDL as the direct substrate, aligned single crystal Pt nanowires were in-situ grown onto the surface. The growing process was achieved at room temperature. At such a low temperature, the reduction rate was dramatically reduced. For the face centered cubic (FCC) structures of Pt, the sequence for the surface energies is increased as {111} < {100} < {110} [30]. According to the lowest energy principle, at the very low reduction rate, the close-packed <111> direction has the largest growth rate with the maximum expression of {111} facets to minimize the total surface energy for Pt FCC structures, finally leading to the formation of 1D single-crystalline nanowires. On the GDL surface, a 3D nanostructure was finally formed with the catalyst layer consisting of a monolayer array of single crystal Pt nanowires with a diameter of 4 nm and length of 100-150 nm [35]. Pt nanowires showed a very good contact with the substrate and can be retained even in the strong sonication treatment. This GDL with aligned nanowires can be directly used as the GDE in PEMFCs. Compared with the dispersed Pt/C process for the fabrication of electrodes, this direct Pt nanowire GDE process is completed in one-step without free nanoparticles produced during the whole procedure (Pt nanoparticles could be cytotoxicity causing negative impact to human health [36]), removing also the steps of supporting Pt on carbon, catalyst ink making and coating process, making the electrode fabrication process much simpler and easier to be scaled up.

Different from the NSTF catalyst, no regular pores formed due to the really small Pt nanowires. It is a highly open 3D structure within the catalyst layer, together with the relative hydrophobic Pt surface (*cf.* PtCoMn and PtNi in the NSTF catalysts), the produced water is still easily to be repelled out and not accumulated to form continuous channels for ion transfer. This means

the degradation induced by local water flooding and accelerated catalyst decay in the NSTF catalyst are mitigated here. However, this also means that proton conducting ionomer is still required to build ion transfer network to achieve high power performance [37]. The comparison with a conventional Pt/C electrode demonstrated that a higher ionomer loading was required for the Pt nanowire electrodes to achieve the best power performance due to the enhanced open structure in the aligned Pt nanowire catalyst layer. The using of ionomer in the catalyst layer also increased the degradation possibility of the electrodes due to the decay of the ionomer or its contact with nanowire surface in fuel cell operation, which could lower power performance in long-term operation. This poor contact between ionomer and Pt nanowires was also confirmed by electrodes from single crystal Pt nanowires supported on carbon (PtNW/C). Li et al [38] built a 1.5 kW PEMFC stack using PtNW/C as cathode catalysts and compared with conventional Pt/C nanoparticle catalysts. To evaluate the stability of the Pt nanowire catalysts in real-life context operation, they conducted a 420 h dynamic drive cycle durability test. PEMFC stacks exhibited only a slightly lower performance degradation rate of 14.4% and 17.9% for PtNW/C and Pt/C based cathodes, respectively. Considering the outstand stability of Pt nanowire itself, the TEM image and particle size histogram analyses were conducted to the cathode catalysts before and after the durability testing. Fig. 7 depicts minimal changes observed with the PtNWs compared with severe Pt nanoparticle growth and aggregation for Pt/C after the durability testing. The very little degradation of the PtNW catalyst further demonstrates its excellent stability, and also indicates the degradation of the Pt nanowire-based electrodes can be ascribed to the electrode structure decay, i.e. the declined contact between ionomer and PtNWs, and the decay of ionomer itself, which finally results in the performance drop. So, to address the durability challenges with the fuel cell electrodes, a fundamental understanding of the adhesion of ionomer with various catalyst surface is required.

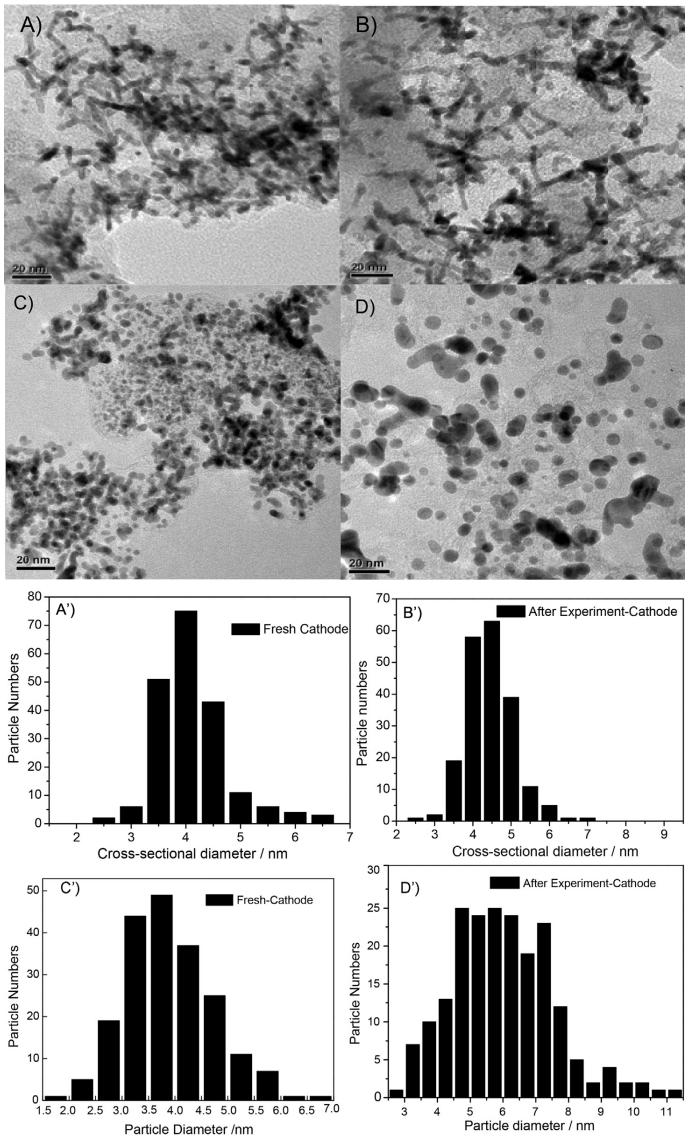

Fig. 7. TEM images and particle size histograms of the cathode PtNW/C and Pt/C before ((A) and (A'), (C) and (C')) and after ((B) and (B'), (D) and (D')) 420 h durability testing, respectively. Reproduced from Ref. [38] with permission of Elsevier, 2015.

As the electrode with a monolayer array of Pt nanowires within the catalyst layer, an optimal Pt nanowire distribution density determined by the Pt loading is key to achieve PEMFCs with high power performance. An increased catalyst loading can lead into a higher power performance, but too high the Pt loading has a trend to form Pt nanowire agglomerates and reduce the catalyst utilization ratio in the electrode (Fig. 8) [39]. Therefore, to attain a high

catalyst utilization ratio at a large catalyst loading, the electrode with uniform distributed aligned Pt nanowires with little or even no agglomerates is highly preferred.

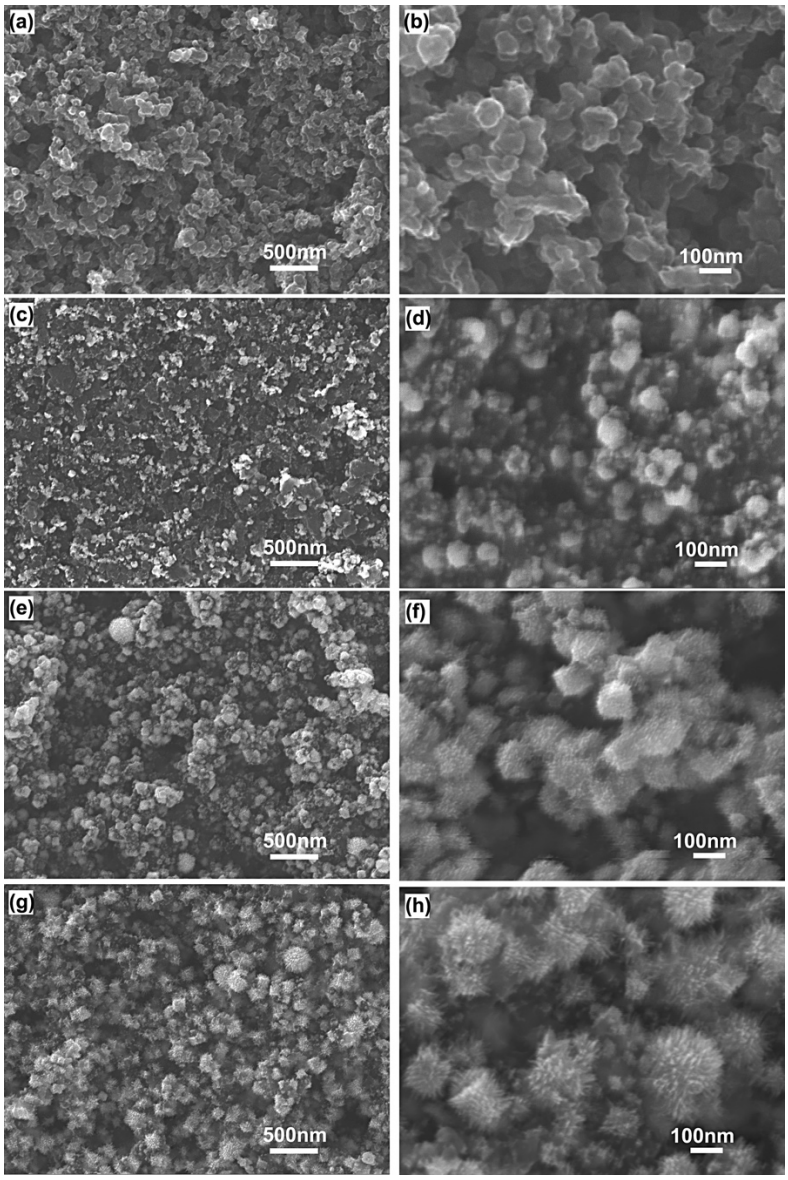

Fig. 8. SEM images of plain GDL surface ((a) and (b)) and Pt nanowire GDEs with various catalyst loadings at 0.1 ((c) and (d)), 0.5 ((e) and (f)) and 1.0 mg cm^{-2} ((g) and (h)). Reproduced from Ref. [39] with permission of Elsevier, 2012.

To prevent water flooding in PEMFC operation, the GDL is usually treated with polytetrafluoroethylene (PTFE) polymer to get super hydrophobic surface, which thus facilitates the repelling of the generated water and keep the smooth diffusion of the reactant

gas to catalyst surface. However, this super hydrophobic surface is highly non-wettable to the aqueous reaction solution in the formic acid reducing process. The inert GDL surface provides very limited nucleation sites, thus many nanowires tend to grow from one crystal nucleus on the GDL surface finally forming very large agglomerates of nanowires (Fig. 8(e) and 8(g)). To address this challenge, a few techniques were employed in our group to improve the nanowire distribution within the aligned Pt nanowire electrode.

To understand the influence of the GDL surface properties on the growth of aligned nanowires, a systematic investigation was conducted to evaluate the evolution of the GDL structure including the top microporous layer (MPL) and the carbon fibre substrate [40]. The results demonstrated that, to achieve a GDE with high power performance, it was critical to control the amount of nucleation sites on the MPL surface for the growth of uniform Pt nanowires with a balanced mass transport loss. The obtained optimum carbon loading in the MPL was 4 mg cm^{-2}, as a higher carbon loading resulted in a very thick MPL and a smaller carbon amount could not cover the surface very effectively. Regarding the carbon composition in the MPL, the mixture of carbon black (CB) 50% and acetylene black (AB) 50% provided a suitable porosity and a reasonable number of surface nucleation sites for the growth of aligned Pt nanowires to achieve a high power performance electrode. A higher CB amount made nanowires grow into the inner pore surface between the active CB spheres in the MPL, while a higher AB content resulted in agglomerates and sparse distribution of nanowires owing to the inert surface properties. Furthermore, the PTFE amount within the MPL needed to be kept as low as possible to enable effective nucleation sites on the surface while could still prevent water flooding during fuel cell operation.

In the synthesis of nanostructures, reaction temperature has been regarded as an important controlled factor. Controlling temperature has been confirmed as a good tool to tune the phase formation kinetics and the driving force for mass transfer, thus changing the morphology and property of the product. With the aligned Pt nanowire electrode, the synthesis temperature

was finely tuned for simultaneously controlling the behaviour and structure of nanowires for practical applications (Fig. 9) [41]. At a low temperature (e.g. 15°C), the main structures obtained were huge Pt nanowire agglomerates with a low catalyst utilization and poor power performance. An increased temperature led to improved distribution of Pt nanowires on the support surface. However, too high the reaction temperature (i.e. 50°C) resulted in the formation of 0D catalyst nanoparticles in solution. An optimal temperature was found at about 40°C, when uniformly distributed aligned Pt nanowires were achieved on the GDL surface, showing the best catalytic performance in H_2/air fuel cell test. Benefiting from the enhanced intrinsic catalytic activity of Pt nanowires and the improved mass transfer performance of the aligned nanowire electrode, a higher power density of 0.82 W cm^{-2} was obtained (at 0.6 V) compared with 0.74 W cm^{-2} of the commercial Pt/C catalyst (TKK). The in situ H_2/O_2 testing demonstrated a double mass activity and a three times higher specific activity of Pt nanowires over Pt/C. The aligned Pt nanowire electrode also exhibited a better durability than the one with Pt/C nanoparticles, demonstrating 48% and 67% ECSA losses after the durability test, respectively.

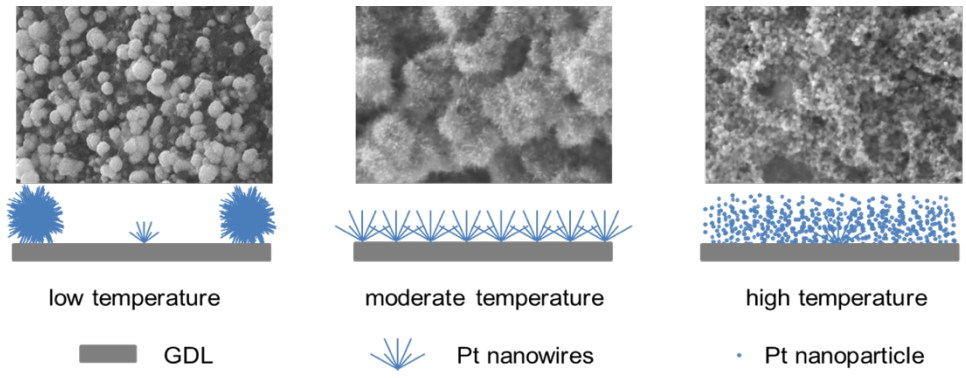

Fig. 9. Schematic diagram for Pt nanostructures grown on carbon paper GDL surface at (a) low, (b) moderate and (c) high temperatures. Reproduced from Ref. [41] with permission of Elsevier, 2015.

Although the controlling of the reaction temperature at 40°C can effectively improve the Pt nanowire distribution, the small temperature window brings big difficulties in the practical

electrode fabrication process. Other surface modification technologies are required to improve the nanowire growth at room temperature. Pd has been used as nanoseeds to control the growth of three-dimensional (3D) Pt-on-Pd bimetallic nanodendrites supported on graphene nanosheet, since it can be easily reduced because of the higher standard reduction potential (*cf.* Pt) [42-44]. Furthermore, the hybrid with Pd can also potentially increase the catalyst activities and stability of Pt. Therefore, Pd nanoseeds were introduced onto the GDL surface to improve the growth of Pt nanowires [45]. The results demonstrated that an optimal amount of Pd (i.e. 5 at%) led to more uniform distributed PtPd nanostructures on a 16 cm^2 GDL, but the length of the nanowires reduced to 5-20 nm to form nanodendrites on the GDL surface. The better distribution improved the power density from 0.64 to 0.73 W cm^{-2} at 0.6 V, and ECSA from 14.70 to 22.40 m^2 g^{-1} measured in the cathode. However, the durability test demonstrated a larger drop in the power density for aligned PtPd nanodendrite electrodes, showing a degradation ratio of 20.1% compared to 12.7% of the aligned Pt nanowire electrode. Considering the confirmed enhanced stability of PtPd hybrids over Pt, this larger degradation ratio can also be ascribed to the declined contact between the electrode ionomer and catalyst nanostructures due to the different surface properties of PtPd nanodendrites and Pt nanowires, but the detailed mechanism still needs further confirmation.

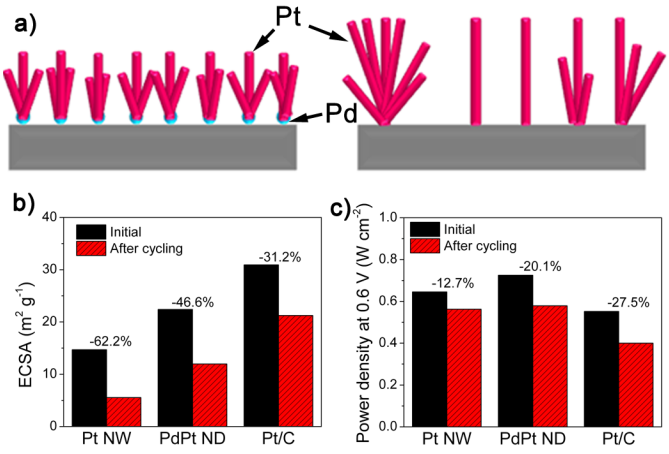

Fig. 10. (a) Schematic of introducing Pd nanoseeds to control the growth of aligned Pt nanowires. Comparison of (b) ECSAs and (c) power densities at 0.6 V for GDEs from PtPd

nanodendrites with 5 at% Pd, Pt nanowires and Pt/C nanoparticles before and after the durability test. Reproduced from Ref. [45] with permission of Elsevier, 2016.

The introducing of Pd seeds improved the distribution of the aligned Pt nanowires, but also resulting in the fast degradation and then plasma surface treatment was introduced. Plasma surface modification is well known as an economical technology to modify solid surfaces before further processing, considering the low treatment temperature requirements in the applications, active screen plasma nitriding (ASPN) was introduced to activate the GDL surface for nanowire growth [46,47]. Not like the oxidation activation using strong acids which can destroy the surface properties of pores through the whole GDL, ASPN only modifies a very top surface, usually superficial 5–50 nm, and the dimensions and bulk features of the GDL are kept intact. The ASPN activation was conducted at 120^{o}C for 10 min at 2 mbar (200 Pa) under a gas mixture of N_2/H_2. The treatment successfully introduced various functional groups, e.g. C-N, C=N and O-H on the support surface, increasing the surface activities and facilitating the formation of Pt nuclei thus enabling a uniform growth of aligned Pt nanowires on the GDL surface (Fig. 11(a) to 11(c)). The surface nitriding effectively reduces the huge agglomerates formed in the catalyst layer for an improved catalyst utilization. Furthermore, the ASPN process introduced N-doping and more defects to the support surface. These defects confined the Pt atoms in reaction to form tiny nuclei, resulting in the growth of ultrathin Pt-nanowires with diameters of 2.5–3.0 nm (Fig. 11(d) to 11(f)). The reduced diameter increased the metal surface area, leading to an ECSA as large as that of Pt/C nanoparticle electrodes. The enhanced catalyst utilization and ECSA finally led to an improved power performance. The test as the cathode in direct methanol fuel cells (DMFCs) demonstrated that with a half Pt loading, the MEA with the Pt nanowire cathode (2 mg_{Pt} cm^{-2}) showed a power density of 64 mW cm^{-2} at 0.4 V compared to 47 mW cm^{-2} of that with the Pt/C electrode (4 mg_{Pt} cm^{-2}).

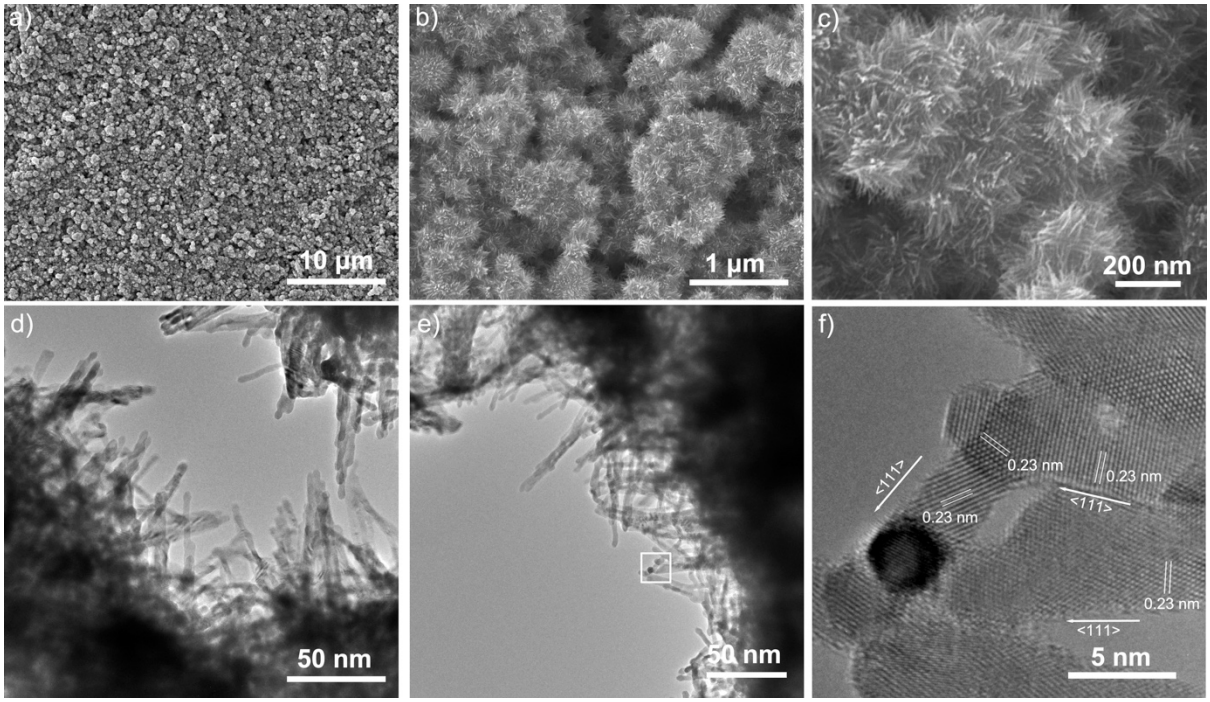

Fig. 11. Images of Pt-nanowires grown on the plasma activated GDLs. (a–c) SEM images of a 3D nano-architectured catalyst layer with aligned Pt nanowires in-situ grown on the activated GDL support surface, at three different magnifications. (d–f) TEM and HR-TEM images of Pt-nanowires in the nano-architectured catalyst layer. (f) shows a HR-TEM image of the part specified by the white square in (e), indicating the single-crystal nanowires with the growth direction along the <111> axis. Reproduced from Ref. [46] with permission of Springer Nature, 2014.

4.2.2 Catalyst coated membrane from aligned single crystal Pt nanowires

Compared with GDE method, catalyst coated membrane (CCM) or decal approaches have a good potential to fabricate MEAs with higher power performance due to the better contact between the catalyst layer with PEM [2]. For GDEs from aligned single crystal Pt nanowires, the uneven surface of the MPL within the GDL (Fig. 5(a), 8(a) and 8(b)) makes the top of the aligned nanowires not in a horizontal plane, thus when being hot pressed onto PEM, not all of them will build a good contact with the PEM even after a thin layer of proton conducting

ionomer is coated on the GDE surface. But, if the aligned nanowires can be in-situ grown on the flat PEM or decal substrate surface, this situation will be improved.

As the commonly used membrane in PEMFCs, Nafion membrane is the combination of a stable PTFE backbone with acidic sulfonic groups. It is very difficult to form uniformly distributed nucleation sites on the PEM surface to grow aligned nanowires due to the inert backbone. To overcome the challenge, our collaborator Sui's group introduced a thin carbon powder matrix on PEM surface as a functional layer to grow aligned Pt nanowires. This carbon matrix surface plays the same role as the MPL in the GDL for the nanowire growth, but it is much flatter due to the even PEM surface with the thin matrix [48,49]. The same formic acid reduction method was then deployed to grow aligned Pt nanowires onto the matrix. PEM coated with the matrix and aligned nanowires were then directly used as the half-MEA for PEMFC test. The carbon matrix thickness, proton conducting ionomerin catalyst layer and Pt nanowire loading were also optimized based on the power performance [50,51]. The results demonstrated the importance to control the structure to maximize TPB within the catalyst layer, including (i) with a thinner carbon matrix, Pt nanowires had a uniform distribution across the catalyst layer cross-section, but locally agglomerated into large size superstructures which blocked the pores. However, with a thick matrix layer, Pt nanowires showed a gradient distribution through the catalyst layer resulted in a low catalyst utilization; (ii) a higher Pt loading caused heavy agglomeration of Pt nanowires resulting in a decrease of the ECSA and an increased mass transport limitation. A Pt loading of 0.30 mg cm^{-2} and carbon powder loading of 0.10 mg cm^{-2} in the matrix were obtained with optimal performance for PEMFCs; and (iii) the optimal ionomer contents in the carbon matrix and impregnated on the surface of the aligned Pt nanowires were 10 wt% of the carbon matrix and 8 wt% of the Pt loading, respectively. The ionomer content in the carbon matrix had a great influence on the agglomeration and distribution of Pt nanowires grown on it, and therefore influenced the cell performance. Impregnated ionomer on the surface of the aligned Pt nanowires improved the ionic conductivity but excess ionomer limited the mass transport characteristics. The Pt/C

nanoparticle electrocatalyst was also introduced to replace the carbon powder in the matrix [52]. It was found that the Pt nanoparticles in the matrix served as crystal seeds and growth sites for nanowire growth. A reduced optimal Pt loading of 0.20 mg cm^{-2} is obtained, but the Pt/C matrix finally led to a worse crystalline, short length and lower catalyst activity of Pt nanowires obtained than those with the carbon matrix.

To further improve the contact between the Pt nanowires and PEM, decal method was then introduced to grow aligned Pt nanowires [53-55]. The carbon matrix was coated onto a transfer substrate followed by the same formic acid reduction method to grow nanowires. The structure was then transferred to PEM to fabricate MEAs. It was found that the introduction of only a small amount of Pt/C in the carbon matrix played a positive effect here, facilitating the growth of uniform aligned Pt nanowires. An optimal Pt/C loading was found to be 5 μg_{Pt} cm^{-2} with a carbon loading of 0.02 mg cm^{-2} in the carbon matrix. The optimal cathode with total Pt loading of 0.205 mg cm^{-2} (5 μg_{Pt} cm^{-2} with Pt/C and 0.2 mg_{Pt} cm^{-2} with the aligned Pt nanowires) showed the highest specific current density of 89.56 A g_{Pt}^{-1} at 0.9 V under H_2/air feeding (Fig. 12), which was about 110% higher than that of the commercial GDE with a Pt loading of 0.40 mg cm^{-2}, demonstrating a high potential of this approach.

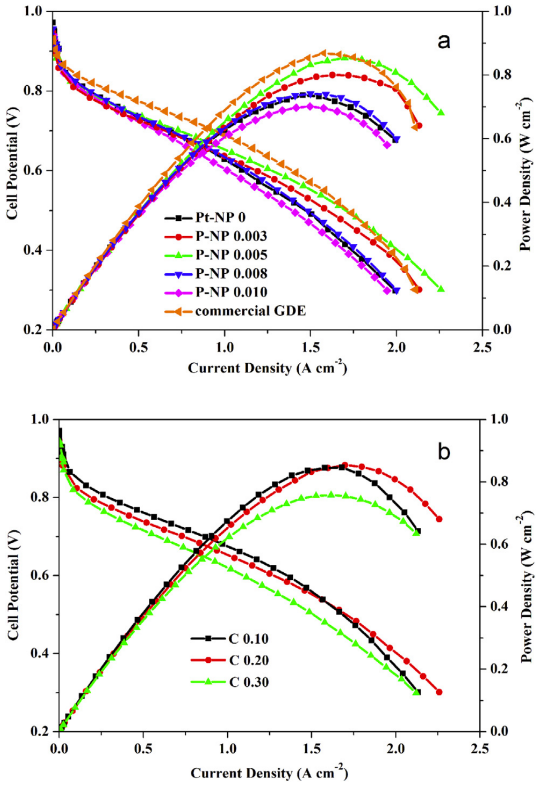

Fig. 12. Polarization and power density curves of the commercial GDE, the Pt nanowire cathodes with various Pt/C loadings from 0 to 0.010 mg_{Pt} cm^{-2} in (a), and various carbon loading of 0.10, 0.20, and 0.30 mg_C cm^{-2} in (b), respectively. The deposited Pt loadings for all samples are 0.20 mg_{Pt} cm^{-2}. The carbon loading (a) and Pt/C loading in (b) are 0.02 mg_{Carbon} cm^{-2} and 0.005 mg_{Pt} cm^{-2}, respectively. Reproduced from Ref. [55] with permission of Elsevier, 2018.

4.3 Electrodes from aligned Pt-based nanotubes

As 1D nanostructures, Pt-based nanotubes also owe similar advantages to nanowires and suffer less from dissolution, aggregation and Ostwald ripening compared to Pt nanoparticles. Furthermore, nanotubes have a potential to provide a high surface area and be easier prepared at alloy form for enhanced catalytic activities. In this case, aligned Pt and Pt alloy nanotubes have also been explored for PEMFC applications.

Morin et al. prepared aligned Pt-based nanotubes using a sacrificial template of porous Anodized Aluminum Oxide (AAO). Pt was deposited onto the inside wall of AAO pores using atomic layer deposition (ALD) [56] or electron beam evaporation (EBE) [57] technique. The Pt coated AAO template was then decal transferred to PEM surface by hot pressing followed by removing the AAO template using NaOH. With this approach, depending on the pore size of the AAO template, aligned Pt nanotubes with an external diameter of around 150-180 nm and 20 nm thick Pt walls were achieved. The large diameter resulted in a small ECSA although a higher surface utilization (160% *cf.* Pt/C). To increase the surface and mass specific activity, they developed aligned PtCu nanotubes by galvanic displacement reaction between chloroplatinic salt and copper nanowires grown into the porous AAO template [58]. A 2 μm thick catalyst layer was obtained consisting of an array of aligned nanotubes of 30 nm in diameter, with an average distance of 60 nm (about 32 billion nanotubes per cm^2). The wall of nanotubes was made of PtCu alloy nanoparticles of 3 nm in diameter (reaching a roughness factor of 220 cm^2_{Pt}/cm_{geo}^2 with a loading of 0.15 mg_{Pt}/cm_{geo}^2). The specific activity obtained for such structure was demonstrated ten times higher than Pt/C catalyst (2.2 mA cm^{-2}_{Pt}) in real operating conditions.

Rather than using the sacrificial AAO template, open-walled PtCo bimetallic nanotube arrays were constructed through a hydrothermal and PVD method for PEMFC applications [59]. Highly ordered Co-OH-CO_3 nanowire arrays (NWAs) were prepared as the template, then Pt layer was coated onto Co-OH-CO_3 NWAs by magnetron sputtering. Pt and Co were alloyed by thermal annealing, endowing the catalyst layer with extra electro activity. Then the template was removed by acid wash. The process was schematically shown in Fig. 13. A catalyst layer with a thickness ca. 300 nm was achieved with aligned open-walled PtCo bimetallic nanotubes with a diameter ca. 100 nm and skin thickness estimated to be ca. 17 nm. Serving as cathode, a 1.7 fold higher Pt-based specific power density (14.38 kW g_{Pt}^{-1}) was obtained than the conventional CCM based on Pt/C electrocatalyst. However, the using of toxic NH_4F in the preparation Co-OH-CO_3 NWAs partially lowers the potential of this process.

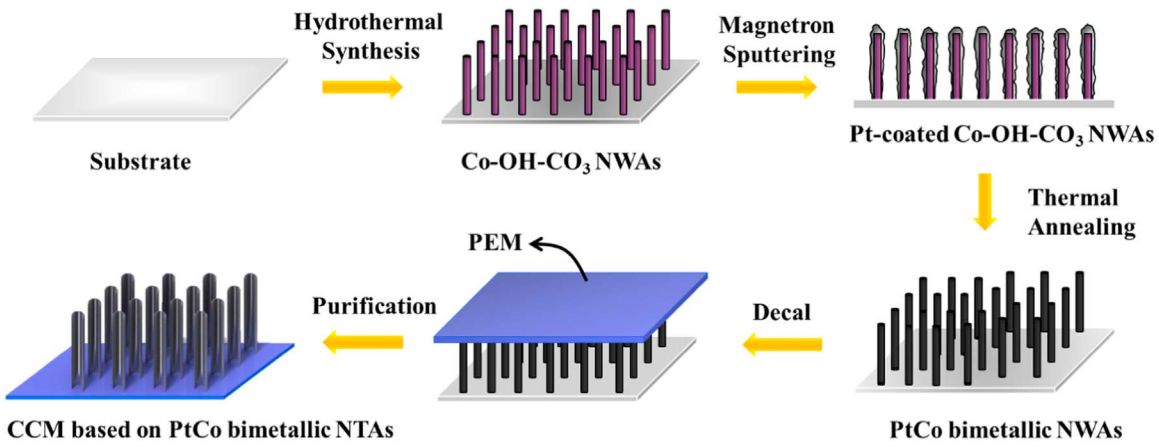

Fig. 13. Schematic illustration of the fabrication process of CCM based on aligned PtCo bimetallic nanotubes. Reproduced from Ref. [59] with permission of Elsevier, 2017.

5. Perspective and conclusions

This review describes the recent advance in catalyst electrodes made of aligned 1D nanostructures for PEMFC applications. Significant progresses have been achieved from the earliest NSTF catalyst layer, to Pt nanoparticles decorated carbon and TiO_2 nanotubes arrays, and to self-standing catalysts from aligned Pt nanowires and nanotubes. The extremely thin catalyst layer, together the vertically oriented structure enabling better mass transportation in practical electrodes for a super-high degree of active site exposure and catalyst utilization. Outstanding catalytic performance and durability were observed, and the big potential is demonstrated for PEMFC applications.

The ultrathin jagged single crystal Pt nanowire has been demonstrated as the most promising catalyst materials up to now, and lots of research groups and fuel cell manufactures are working on it with an expectation to scale up the process for the development of next generation PEMFCs. A breakthrough is urgently required to fully transfer the superior performance of jagged Pt nanowires to working electrodes to realize the dream of PEMFCs operated at a high power density with long-term durability. The concept of 3D electrodes from aligned nanowires fits the jagged Pt nanowires perfectly, but the challenges with the current

preparation process limit further progress. Aligned Pt-transitional metal alloy nanowires need to be prepared at first before the transitional metal can be fully leached to achieve jagged Pt nanowires. With the current oleylamine process, both the preparation and separation procedure are too complex and less effective to fulfil the practical requirements for PEMFC applications. Furthermore, it is extremely difficult to grow aligned nanowires on the substrate with the oleylamine process limited by the synthesis principles.

The simplicity and green preparation process make the formic acid reduction to fabricate aligned Pt nanowire electrodes a promising approach for prepare high power performance MEAs by the roll-to-roll processing. Based on our progress in the modification of the substrate surface to improve the distribution of aligned Pt nanowires, e.g. ASPN activation, more techniques are still required to precisely control the nanowire distribution to form well designed 3D structure to accurately tune the catalyst exposure and mass transfer behaviour within the catalyst layer. To further improve the 3D structured electrodes, a fundamental understanding of the structure-property relationship is necessary in particular with help from the numerical simulation techniques. Another major direction is to increase the ECSA of the aligned single crystal Pt nanowires, either by reduced the diameter to prepare ultrathin Pt nanowires, or to make jagged single crystal Pt nanowires. The in-situ growth of aligned nanowires by the formic acid reduction method shows some potential for the fabrication aligned ultrathin jagged Pt nanowires. However, a slow reduction rate is required to form Pt nanowires with the weak reductant (e.g. formic acid) at near room temperature, and the reducing potential of the formic acid is not strong enough to also simultaneously reduce the transitional metal ions to achieve single crystal Pt alloy nanowires. Our group tried impregnated Ni precursor onto the aligned Pt nanowire surface followed by H_2 reduction to fabricate PtNi nanowires [60], but it was found that the ultrathin Pt nanowires could not stand the high reduction temperature required for the Ni alloying. Hydrothermal reduction process on metal substrate (e.g. SS or Al) combined with decal transfer approach exhibits a possibility for this application, but the feasibility still needs experimental confirmation and the scale up is also a big challenge.

The NSTF catalyst layer is one important approach for the development of aligned 1D nanostructure electrodes. Combined with the PVD method, it has been confirmed as a technique to fabricate MEA based on a roll-to-roll process. A further development of this process is partially limited by the corrosion of support polymer material in long-term operation, as a consequence a thick catalyst layer near 10 nm is required to coat the whole polymer whisker surface, together with the large size of the polymer whisker supports, finally resulting in a low ECSA. Furthermore, with the PVD technique, as a roll-to-roll process used for catalyst deposition, arrays of large crystalline catalyst nanowhiskers are usually obtained along the polymer whiskers, and therefore alloy catalysts are required to increase the specific surface activity to compensate the low ECSA. The hydrophilic Pt alloy surface and nanowhisker array morphology together cause heavy water flooding in high current density operation in PEMFCs. Despite 3M Co. has introduced some techniques, e.g. a gradient anode GDL structure to partially release the generated water, there is still a lot of efforts required to finally address these big challenges.

Electrodes from Pt nanoparticles decorated aligned 1D supports, including aligned CNTs, TiO_2 nanotubes and nanorods were hot topics in PEMFC research, but further breakthroughs are necessary to simplify the complex preparation process, and also address the poor intrinsic conductivity of the metal oxide supports. To keep a good dispersion and prevent the aggregation of the catalyst nanoparticles, a very low catalyst loading is usually required. To overcome this drawback and the poor stability of the extremely small catalyst nanoparticles, the replacement with 1D Pt nanostructure catalysts is a solution. However, the advantage is still not very clear compared with the electrodes from the self-standing aligned 1D catalyst nanostructures. The electrodes from the self-standing catalyst nanotubes are still limited by the large thickness of nanotubes and the complex process based on the template approach. The development of extremely thin nanotubes can potentially increase the catalytic activities but further strategies are then required to address the resulted poor mechanical strength.

In addition to the research work on novel catalyst nanostructures and electrode fabrication techniques, the surface and structure modification of catalysts and electrodes were also studied in recent years, in particular the using of protic ionic liquids (ILs). The excellent oxygen solubility and diffusivity of ILs can help maximize the contribution of active catalyst sites within the mesopores of catalyst nanostructures, which are too small to be penetrated by the large polymer clusters of the proton conducting ionomer (e.g. Nafion) [61], thus increase the catalyst utilization ratio in electrodes. Furthermore, the hydrophobicity of ILs can protect the catalyst surface from a direct contact with the acidic water in fuel cell operation [28,62], and help limit produce water build up on the exterior of the catalyst, lowering its effect on the mass transport of reactant O_2 [63]. Although the enhancement mechanisms of the IL modification for catalysts in PEMFCs are still in debate, the positive effects have been confirmed. Especially, the positive effects from the surface protection and access to mesopores make the IL modification an ideally approach to modify low cost highly porous non-platinum group metal (non-PGM) catalysts (e.g. FeCN and CoCN deduced from MOF) for PEMFC applications, which can help address the major challenge of the poor stability due to the corrosion in the acidic operation environment.

Proton conducting ionomer in the catalyst layer plays a significant role on the electrode performance. For 1D nanostructures and even aligned nanowires, the surface contact with ionomer could be much different from that with conventional Pt/C nanoparticles. Furthermore, because of the thin catalyst layer with the aligned 1D nanostructured electrodes, the volume water generation rate will also be much higher (20 to 30 times) than the Pt/C electrodes in PEMFC operation. Therefore, ionomer can have a much different behaviour, including distribution, expansion and shrinkage, degradation. A thoroughly study of the ionomer contact on various catalyst nanostructures by probing the intermolecular and interfacial forces using various nanomechanical tools and methodologies [64], and monitoring the behaviour of ionomer in fuel cell operation will provide valueless reference for the design and development of high power performance 3D nanostructured electrodes from aligned 1D catalysts.

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